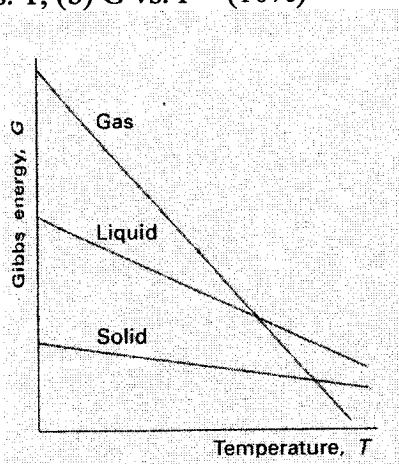
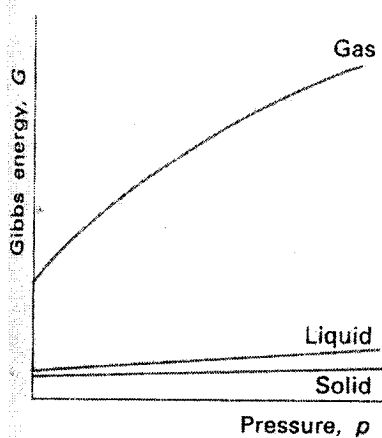


高等 物理化學 資格考

- The π electrons of metal porphyrins, such as the iron-heme of hemoglobin or the magnesium-porphyrin of chlorophyll, can be visualized using simple model of free electrons in a two-dimensional box.
 - Obtained the energy levels of a free electron in a two-dimensional square box of length a .
 - For a porphyrin-like hemin that contains 26 π electrons, sketch an energy-level diagram for the occupied orbitals (Hint: degeneracy).
 - The porphyrin structure measures about 1 nm on a side ($a = 1$ nm). Calculate the longest-wavelength absorption band position for the molecule. (15%)
- Using Hückel molecule-orbital theory, determine whether the linear state or the triangular state of H_3^+ is the more stable state. Repeat the calculation for H_3 and H_3^- . (10%)
- The bond length in $^{12}C^{14}N$ is 117 ppm and its force constant is 1630 N/m. Predict the vibrational-rotational spectrum of $^{12}C^{14}N$. (Hint: P, Q and R bands) (10%)
- The rate law for the reaction described by $[N_2O_2(g) \rightarrow 2 NO(g)]$ is first order in the concentration of $N_2O_2(g)$. Derive an expression for the time-dependent behavior of $[NO]$, the product concentration. (8%)
- The rate constant for the reaction $[2 HI(g) \rightarrow H_2(g) + I_2(g)]$ is $1.22 \times 10^{-6} \text{ dm}^3/\text{mol}\cdot\text{s}$ at 575 K and $2.50 \times 10^{-3} \text{ dm}^3/\text{mol}\cdot\text{s}$ at 716 K. Estimate the value of E_a from these data. (7%)
- Put 1 mole of O_2 in a 1 liter container A, and 5 moles of N_2 in a 2 liter container B. Both A and B are kept at 300K, and are connected with a valve. When the valve is opened to allow the mixing of gases, please calculate (a) ΔS (b) ΔG (20%)
- Melting point of Naphthalene is 80.2°C , vapor pressure of its liquid is 10 torr at 85.8°C , 40 torr at 119.3°C . Please use the Clausius-Clapeyron equation to calculate (a) normal boiling point of Naphthalene, (b) $S_{\text{vaporization}}$ at b.p. (20%)
- Please use thermodynamic functions to explain the difference in slopes for three phases in (a) G vs. T ; (b) G vs. P (10%)



(a)



(b)